

## **Properties of High-Efficiency CIGS Thin-Film Solar Cells**

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# PROPERTIES OF HIGH-EFFICIENCY CIGS THIN-FILM SOLAR CELLS

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## ABSTRACT

We present experimental results in three areas. Solar cells with an efficiency of 19% have been fabricated with an absorber bandgap in the range of 1.1-1.2 eV. Properties of solar cells fabricated with and without an undoped ZnO layer were compared. The data show that high efficiency cells can be fabricated without using the high-resistivity or undoped ZnO layer. Properties of CIGS solar cells were fabricated from thin absorbers (1  $\mu\text{m}$ ) deposited by the three-stage process and simultaneous co-deposition of all the elements. In both cases, solar cells with efficiencies of 16%-17% are obtained.

## INTRODUCTION

$\text{CuInGaSe}_2$  (CIGS) polycrystalline thin film photovoltaic cells are a realistic option for reaching the goal of low-cost, high efficiency power conversion from renewable energy sources. Several research groups have reported a steady increase in the efficiency of laboratory devices [1-3]. Similar progress has been reported in the manufacturing arena, where the efficiency of champion modules has exceeded 13% and the yield is above 80% [4]. However, there is a large gap between the efficiency of laboratory cells and commercial modules. This can be narrowed by a concerted effort at the fundamental science of thin film materials and interfaces. Historically, the community has concentrated its efforts on the fabrication and physical properties of the materials themselves and much less on the electronic processes that occur at the interfaces. More attention to this area can lead to a simplification of device structure, and improve the stability and yield of the products. At NREL, we have systematically improved the efficiency of the CIGS solar cells fabricated by the three-stage process. Although the deposition method is somewhat difficult to implement in manufacturing, it offers advantages in control of morphology, defects, orientation, bandgap grading, and stoichiometry control. The most efficient CIGS thin film solar cells have been fabricated by the three-stage process. It is now possible to compare the properties of the three-stage devices with those fabricated by other methods and identify areas for improvement.

In this report, we summarize the properties of high efficiency cells fabricated by varying the Ga content of the absorber. Improvement in our understanding of the growth process has resulted in our ability to fabricate solar cells with efficiencies of 18%-19% in the bandgap range of 1.1-1.2 eV. Next, we provide a comparison of the properties of solar cells fabricated using a bilayer ZnO and a

single, conductive ZnO layer. Finally, we present the properties of solar cells fabricated on thin absorbers.

## EXPERIMENTAL

CIGS absorbers were grown on soda-lime glass substrates with a sputter-deposited Mo layer. The absorber is grown by first depositing an  $(\text{In,Ga})_2\text{Se}_3$  layer and reacting it with Cu and Se. Compositional control was achieved by detecting the temperature change of the substrate during Cu-poor to Cu-rich transition at the end of the second stage. The third stage consists of the evaporation of In and Ga in the presence of Se. Thinner CIGS absorbers were deposited by reducing the  $(\text{In,Ga})_2\text{Se}_3$  film thickness and making appropriate modifications to the process. Thin absorbers were also prepared by simultaneous deposition of all the elements in one step. CdS deposition was performed using a solution consisting of 0.0015M  $\text{CdSO}_4$ , 1.5M  $\text{NH}_4\text{OH}$ , and 0.0075M thiourea. The samples were immersed in the bath at room temperature and the temperature of the bath was increased to 60°C. CdS thin films in the thickness range of 50-60 nm were deposited in 16 min. The ZnO layer was deposited in two stages. A 90-nm-thick, undoped layer was first deposited from a pure ZnO target using  $\text{Ar/O}_2$  working gas, and a second layer of about 120 nm was deposited from an  $\text{Al}_2\text{O}_3$  doped ZnO target. The sheet resistance of the bilayer was about 65-70  $\Omega/\text{sq}$ . Ni/Al grids were deposited by electron beam evaporation. A 100-nm thick  $\text{MgF}_2$  film was deposited to serve as an antireflection coating. Current-voltage characteristics of the devices were measured under AM1.5 Global spectrum for 1000  $\text{W/m}^2$  irradiance.

## RESULTS AND DISCUSSION

### High Efficiency Solar Cells

CIGS absorbers with a range of energy gaps were fabricated by adjusting the Ga content of the  $(\text{In,Ga})_2\text{Se}_3$  precursor layer. Compositional depth profiles show that the bandgap is graded through the depth of the film. The energy gap was evaluated from spectral response measurements, and the  $\text{Ga}/(\text{In+Ga})$  ratio was derived from the electron microprobe data obtained using 10-kV beam energy. This is indicative of the average composition in a sample volume of approximately 1  $\mu\text{m}$ . The energy gap ranged from 1.1 to 1.21 eV, and the corresponding  $\text{Ga}/(\text{In+Ga})$  ratios ranged from 0.26 to 0.31. Table 1 shows a summary of the properties of solar cells characterized under standard reporting conditions. Table 2 lists

the ideality factor and the reverse saturation current density of the solar cells.

Table I. Parameters of high-efficiency CIGS solar cells.

Sample Number	$V_{oc}$ (V)	$J_{sc}$ (mA/cm <sup>2</sup> )	Fill factor (%)	Efficiency (%)
S2212B1-3	0.701	34.60	79.65	19.3
S2212B1-4	0.704	34.33	79.48	19.2
S2212B1-5	0.703	34.08	79.23	19.0
S2213A1-3	0.740	31.72	78.47	18.4
S2213A1-4	0.737	31.66	78.08	18.2
S2229A1-3	0.720	32.86	80.27	19.0
S2229A1-5	0.724	32.68	80.37	19.0
S2229B1-2	0.731	31.84	80.33	18.7
S2229B1-4	0.728	31.87	80.16	18.7
S2232A1-3	0.703	33.94	79.67	19.0
S2232A1-4	0.704	33.83	80.09	19.1
S2232B1-2	0.717	33.58	79.41	19.1
S2232B1-3	0.713	33.38	79.54	18.9

Table II. Diode parameters determined from light current-voltage curves.  $J_0$  is the reverse saturation current density, and  $n$  is diode ideality factor.

Device Number	$J_0$ (A/cm <sup>2</sup> )	$n$
S2212-B1-3	$5 \times 10^{-11}$	1.35
S2212-B1-4	$6 \times 10^{-11}$	1.36
S2212-B1-5	$6 \times 10^{-11}$	1.35
S2213-A1-3	$4 \times 10^{-10}$	1.57
S2213-B1-4	$5 \times 10^{-10}$	1.62

The above results suggest that high efficiency CIGS solar cells can be fabricated up to a bandgap of about 1.2 eV. The advantage of using a higher band gap is the higher open-circuit voltage and a lower temperature coefficient. This also offers the possibility to reduce the number of cells in a module. High voltages can be maintained along with high fill factors, and the junctions are characterized by low ideality factors and recombination ( $J_0$ ).

### Simplifying Window Layer Structure

In the fabrication of CIGS solar cells, it is customary to use a high-low, resistivity grading of the ZnO layer. An undoped layer of ZnO (high resistivity) is first deposited on the CdS, and this is followed by the deposition of a doped layer. Maintaining adequate transparency and achieving resistivity control of films sputtered from two separate targets is not a trivial problem. Moreover, it is not clear whether the undoped layer is an essential part of the device and what role it plays in the junction. If it plays an insignificant role, it can be removed. To evaluate this, we have fabricated solar cells using the bilayer ZnO and the doped layer only. Absorbers from five growth runs were used for this purpose. Ten samples of each type were prepared on adjacent parts of the absorbers. Each sample contained five solar cells. Hence, the properties of solar cells with bilayer ZnO could be compared against those with the doped layer fabricated on the same absorber and also against devices fabricated on four other absorber runs. Thus, the distribution of 50 cells of each

type becomes a statistically significant population. Figure 1 shows the distribution of  $V_{oc}$ ,  $J_{sc}$ , and Fill factor.

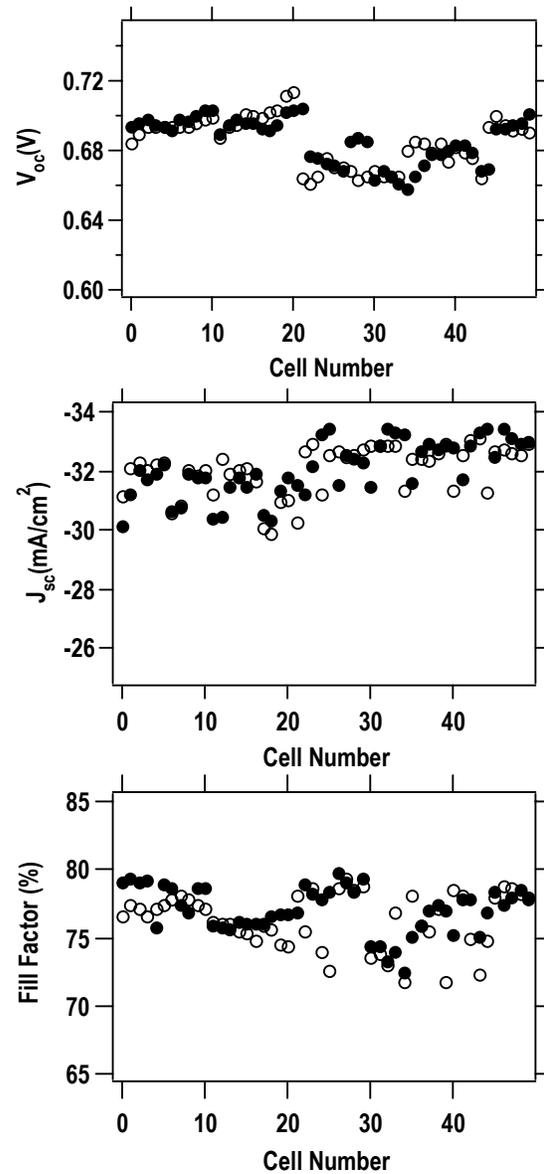


Fig. 1.  $V_{oc}$ ,  $J_{sc}$  and fill factor of CIGS solar cells. Solid circles: doped ZnO layer only; open circles: bilayer ZnO.

An inspection of the data in Fig. 1 reveals that the parameters of the solar cells made without the undoped ZnO layer are identical to those made with the bilayer. It must be pointed out that each sample in this experiment has a spatial variation in the Ga content along its length, and a similar run-to-run variation exists among the five samples. The experiment was repeated on another sample where the CdS layer was deliberately made much thinner than our standard process and similar results were obtained. The average values of  $V_{oc}$ ,  $J_{sc}$ , FF, and efficiency for the two cases are shown in Table 3. No AR coating was deposited on the above samples.

Table 3. Properties of CIGS solar cells with doped ZnO layer and bilayer ZnO. Values for the bilayer are given in parentheses. No AR coating was deposited.

$V_{oc}$ (V)	$J_{sc}$ (mA/cm <sup>2</sup> )	Fill Factor	Efficiency (%)
0.686 (0.685)	32.08 (32.06)	0.77 (0.76)	17 (16.8)

### Thin CIGS Solar Cells

The price and availability of Indium will become dominant concerns for the CIS PV industry when larger-scale production gets under way. One approach to mitigate this would be to reduce the thickness of the absorber layer to a half or quarter of the thickness presently used (2-2.5  $\mu\text{m}$ ). Indeed, several research groups have explored this issue in some detail [5,6]. We have also begun a study of this problem since it has been chosen as a priority research topic for our program. We have made minor modifications to the three-stage process to prepare thinner absorber layers. We have also deposited thin CIGS layers by a single-step co-deposition of all the elements. Absorbers prepared by the three-stage process may be graded band gap materials, whereas co-deposition can provide uniform band gap. A comparison of the materials and devices prepared by the two methods would then allow us to separate out the contributions due to bandgap grading. Fig. 2 shows cross-sectional views of the samples obtained by scanning electron microscopy.

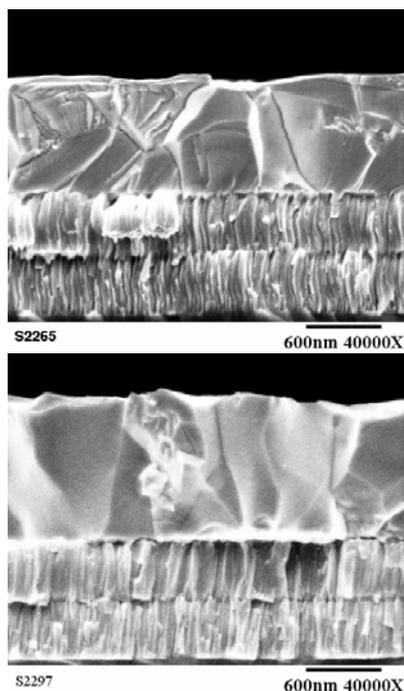


Fig. 2. SEM images of thin CIGS absorbers grown by three-stage (top) and co-deposition (bottom) processes. The bottom layer in each image is a two-layer Mo film.

Solar cells fabricated from the three-stage absorber exhibited open circuit voltages in the range of 650-660 mV, current density of 32-33 mA.cm<sup>-2</sup>, fill factors of 77-78%, and the best conversion efficiency was 16.5%. When we compare the  $J_{sc}$  of these cells with those of the standard cells in Table 1, we find that the current loss due to thinning the cell is about 2-3 mA.cm<sup>-2</sup>. The external quantum efficiency of a solar cell is shown in Fig. 3. The spectral response curve shows a decrease of the long wavelength collection. This is most likely due to incomplete absorption of the long wavelength photons.

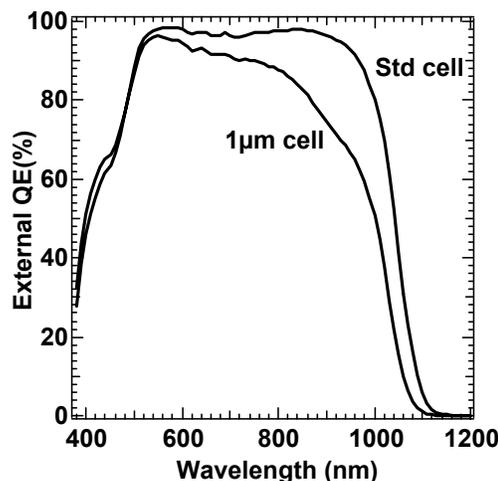


Fig. 3. Quantum efficiency of a thin CIGS solar cell. Also shown is the quantum efficiency of a standard cell.

We have obtained a similar result with absorbers fabricated by co-deposition. The composition of the absorber, determined by electron probe microanalysis was similar to the three-stage absorber. In this case, we obtained an efficiency of nearly 17%. The parameters of the best cells obtained by the two methods are shown in Table 4, below. Further optimization of the growth processes could lead to a higher efficiency. We are also undertaking a study of the recombination processes.

Table 4. Properties of 1- $\mu\text{m}$  thick CIGS solar cells fabricated by three-stage process and co-deposition; the latter are shown in parentheses.

$V_{oc}$ (V)	$J_{sc}$ (mA/cm <sup>2</sup> )	Fill Factor	Efficiency (%)
0.648 (0.703)	32.6 (32.1)	0.78 (0.75)	16.5 (16.9)

### CONCLUSIONS

We have reported the properties of CIGS cells with bandgaps in the range of 1.1-1.2 eV and demonstrated the ability to achieve high efficiency. High open-circuit voltages are obtained in conjunction with high fill factors. A study of the properties of the solar cells with and without the undoped ZnO layer strongly suggests that highly efficient cells can be fabricated without using the undoped ZnO layer even when the CdS layer is made very thin.

This might allow simplification of the device processing. We have also reported high efficiency cells (16%-17%) using CIGS absorbers in the thickness range around 1  $\mu\text{m}$ .

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#### REFERENCES

[1] T. Negami, Y. Hashimoto, and S. Nishiwaki, "Cu(In,Ga)Se<sub>2</sub> thin-film solar cells with an efficiency of 18%," *Solar Energy Materials and Solar Cells*, 67, 2001, pp. 331-335.

[2] K. Ramanathan, M.A. Contreras, C.L. Perkins, S. Asher, F.S. Hasoon, J. Keane, D. Young, M. Romero, W. Metzger, R. Noufi, J. Ward, and A. Duda, "Properties of 19.2% efficiency ZnO/CdS/CuInGaSe<sub>2</sub> thin film solar cells," *Prog. Photovolt: Res. Appl.* 11, 2003, pp. 225-230.

[3] J. Kessler, M. Bodegard, J. Hedstrom, and L. Stolt, "Baseline Cu(In,Ga)Se<sub>2</sub> device production: control and statistical significance," *Solar Energy Materials and Solar Cells*, 67, 2001, pp. 67-76.

[4] D.E. Tarrant, R. Gay, V. Probst, and F. Karg, "CIS thin film development and product status at Shell Solar, May 2003," 3<sup>rd</sup> WCPEC, Osaka, Japan, May 2003.

[5] T. Negami, S. Nishiwaki, Y. Hashimoto, and N. Kohara, "Effect of the absorber thickness on performance of Cu(In,Ga)Se<sub>2</sub> solar cells," *Proceedings of the 2nd WCPEC, Vienna, 1998*; pp. 1181-1184.

[6] O. Lundberg, M. Bodegard, J. Malmstrom, and L. Stolt, "Influence of the Cu(In,Ga)Se<sub>2</sub> thickness and Ga grading on solar cell performance," *Prog. Photovolt: Res. Appl.* 11, 2003, pp. 77-88.

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